

Selective Biomass Conversion Using Silica-Supported Organic Catalysts

Undergraduate Research Thesis

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## **Abstract**

Conversion of biomass to value-added chemicals offers a pathway to creating sustainable, renewable alternatives to historically petroleum-based products. However, many experiments have been conducted to improve the selectivity of biomass conversion, as it is the main challenge for economical and sustainable production. Specifically, experiments have been conducted to increase the selectivity and yield of 5-hydroxymethylfurfural (HMF), a valuable bio-derived chemical, from the dehydration process of fructose. Previous experiments have achieved a high selectivity and yield by reacting fructose in a mixture of water and dimethyl sulfoxide (DMSO) using sulfuric acid as the catalyst, but this method has proven to be impractical. This research tested the hypothesis that the use of a bifunctional catalyst incorporating analogues of  $\text{H}_2\text{SO}_4$  and DMSO in the dehydration reaction of fructose in water would increase the selectivity and yield of HMF. Utilizing the bifunctional catalyst with analogues of  $\text{H}_2\text{SO}_4$  and DMSO in the dehydration reaction of fructose in water yielded approximately 74% selectivity for HMF, an upgrade from conventional dehydration reactions of fructose in water. Overall, this project has shown that it is possible to selectively and efficiently convert fructose to HMF using an environmentally friendly catalyst functionalized with  $\text{H}_2\text{SO}_4$  and DMSO “solvent-like” molecules.

## **Acknowledgements**

I would like to thank Dr. Brunelli, as well as all graduate and undergraduate students in Dr. Brunelli's lab. Specifically, I would like to thank Lagnajit Pattanaik and Mariah Whitaker for conducting catalytic testing for this project, and Lagnajit Pattanaik for conducting background research and creating a number of helpful tables and figures to better understand the project.

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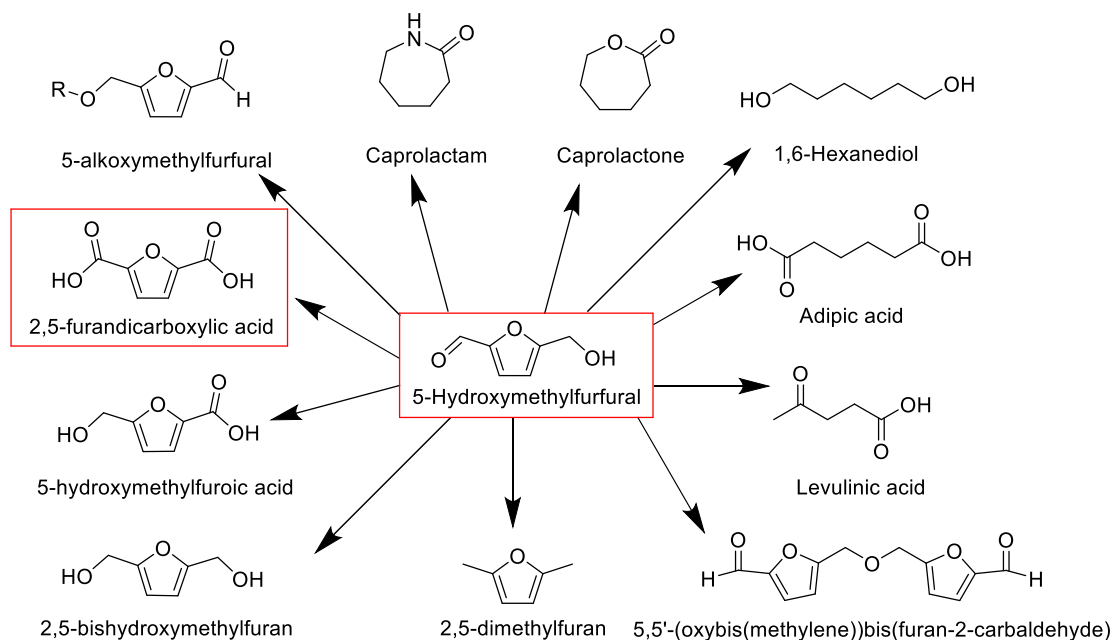
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## 1. Introduction

Creating renewable alternatives to petroleum for producing materials, energy, and chemicals is an important aspect of creating a sustainable planet. Biomass constitutes a sustainable alternative to petroleum and has the potential to decrease the world's dependence on it.<sup>1</sup> HMF, a bio-derived chemical, can be used to synthesize many valuable chemicals that can suffice for other non-renewable chemicals currently used throughout the world.<sup>2</sup> For example, HMF can be used to produce 2,5-Furandicarboxylic acid (FDCA; top 12 priority chemical for energy efficiency and renewable energy<sup>3</sup>). FDCA can be polymerized and has the potential to replace terephthalic acid (PTA), a petroleum-based precursor of polyethylene terephthalate.<sup>3</sup> Figure 1 below shows several of the value-added chemicals that can be derived directly from HMF.

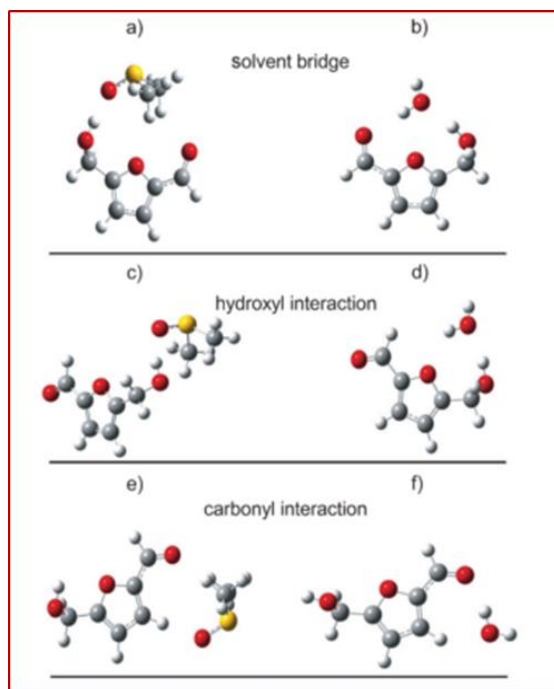


**Figure 1:** Valuable chemicals that can be derived directly from HMF

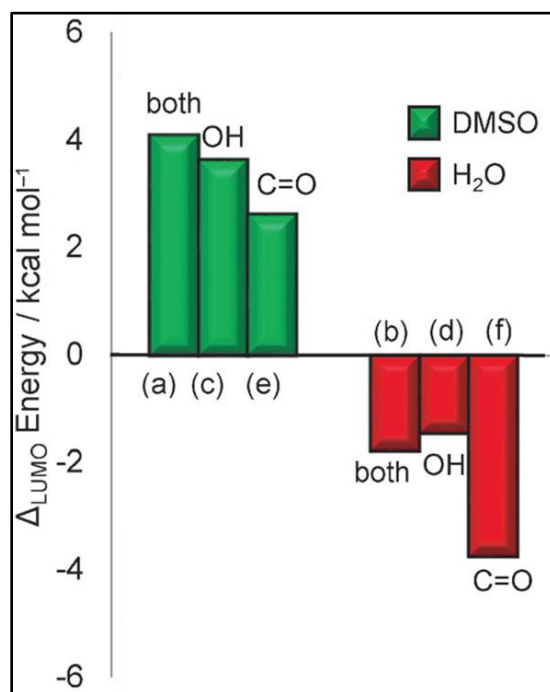
One way that HMF can be synthesized is from fructose in a dehydration reaction.<sup>1</sup> Others have tried to make HMF via this pathway, but have encountered problems with the selectivity and yield of HMF. One method which involves reacting fructose in H<sub>2</sub>O and using

H<sub>2</sub>SO<sub>4</sub> as the catalyst has been found to have a low selectivity and yield of HMF, ranging anywhere from 20-50%.<sup>4,5</sup> Side reactions such as the polymerization to form humins and further rehydration to formic and levulinic acids work to contribute to low yields of HMF under these conditions.<sup>6</sup>

Organic co-solvents with high boiling-points (e.g., DMSO) in an aqueous reaction medium have been found to increase HMF stability by minimizing rehydration and polymerization reactions.<sup>6</sup> The dehydration reaction of fructose in a mixture of DMSO and H<sub>2</sub>O using H<sub>2</sub>SO<sub>4</sub> as the catalyst has been found to have a selectivity and yield over 90% for HMF.<sup>7</sup> High selectivity and yield when using DMSO is thought to be a result of favorable interactions between DMSO and both the carboxyl and hydroxyl groups in HMF. When performing the reaction in a biphasic system, DMSO preferentially solvates HMF over water, increasing HMF's lowest unoccupied molecular orbital (LUMO) energy and preventing further rehydration. These interactions are illustrated below in Figure 2, and the change in LUMO energy when using DMSO as the solvent versus using solely water as the solvent is demonstrated in Figure 3.



**Figure 2:** Interactions of DMSO and water with HMF<sup>6</sup>

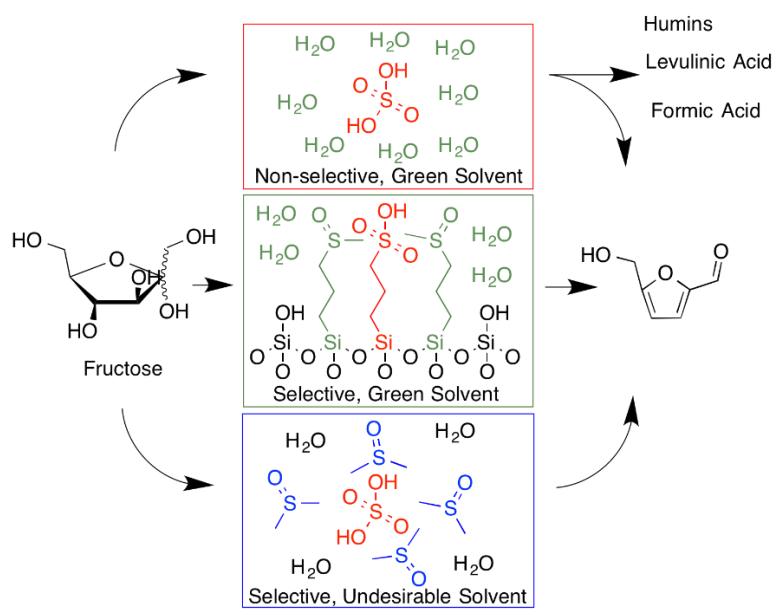


**Figure 3:** Differences in LUMO energy between using DMSO and water as the solvent<sup>6</sup>

However, using DMSO as the reaction solvent has two critical difficulties: (1) HMF has been found to thermally degrade when purified from DMSO, and (2) HMF separation from this

homogenous mixture is an energy-intensive procedure because of the high boiling-point of DMSO.<sup>7</sup> Due to these problems, using this method to produce HMF is undesirable. Moreover, DMSO is an expensive chemical and it cannot be recycled; therefore, this pathway is also uneconomical. As of now, there is not an accepted sustainable process for this reaction.

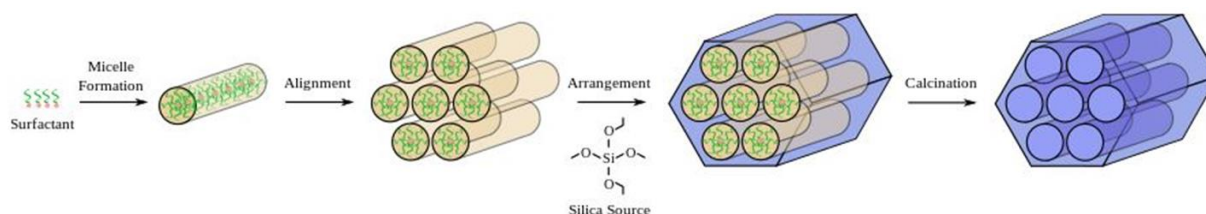
The purpose of this research was to investigate ways to achieve a high selectivity and yield of HMF in the dehydration reaction of fructose in such a way that the HMF can be isolated in an energy-efficient and economical manner. High selectivity and yield of HMF from fructose has been achieved by performing the reaction in DMSO and H<sub>2</sub>O and using H<sub>2</sub>SO<sub>4</sub> as the catalyst, but separating the HMF after reaction completion has been an issue as current separation processes are energy-intensive. This project aimed to achieve a high selectivity and yield of HMF through the use of a bifunctional catalyst. This research tested the hypothesis that the uneconomical process used to separate HMF from the reaction products can be eliminated by using a bifunctional catalyst that incorporates analogues of both the acid, H<sub>2</sub>SO<sub>4</sub>, and organic solvent, DMSO.<sup>1</sup> Figure 4, below, illustrates this hypothesis as well as provides a summary of the previously discussed, unfavorable methods to produce HMF.



**Figure 4:** Potential catalytic pathways for the selective dehydration of fructose to HMF. (Courtesy of Prof. Nicholas Brunelli)

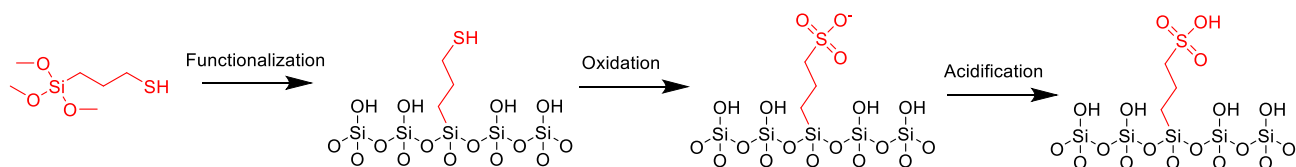
## 2. Materials and Methodology

The three main components to this research project were catalyst synthesis, catalyst characterization, and catalyst testing. Catalyst synthesis first involved creating a bare mesoporous silica by performing a previously verified procedure.<sup>8</sup> Silica is a useful solid support for bifunctional catalysts because it is only slightly acidic and molecules can be easily functionalized onto its surface through two validated methods: post-synthetic grafting or co-condensation.<sup>1</sup> The two most common types of mesoporous silica are SBA-15 and MCM-41. A general illustration of the synthesis of these silica sources is outlined below in Figure 5.



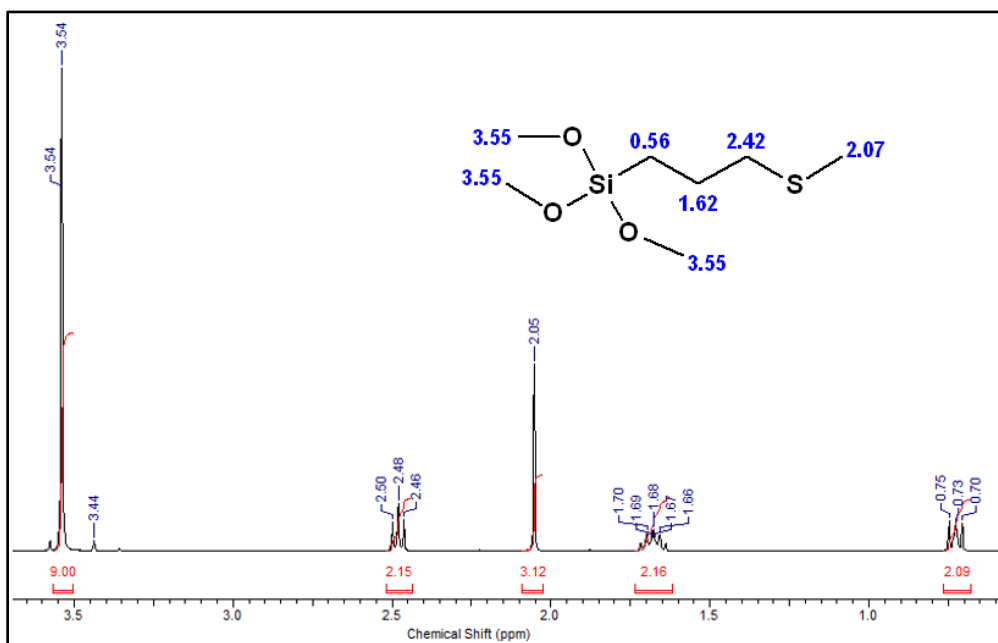
**Figure 5:** Synthesis procedure for mesoporous silica<sup>11</sup>

The second part in catalyst synthesis involved functionalizing silica. Two types of catalysts were produced via functionalization, one with  $\text{H}_2\text{SO}_4$  analogues and one with analogues of both  $\text{H}_2\text{SO}_4$  and DMSO. To prepare the catalyst with only  $\text{H}_2\text{SO}_4$  analogues, a “grafting from” approach was used, where the analogue is synthesized after functionalizing a starting molecule on the silica surface. The synthesized bare mesoporous silica was functionalized with (3-mercaptopropyl)trimethoxysilane, a commercially available organosilane that contains a thiol group. The thiol groups were oxidized using hydrogen peroxide then acidified using aqueous sulfuric acid to produce propylsulfonic acid-functionalized silica (Catalyst 1). The synthesis procedure that was conducted is illustrated below in Figure 6.



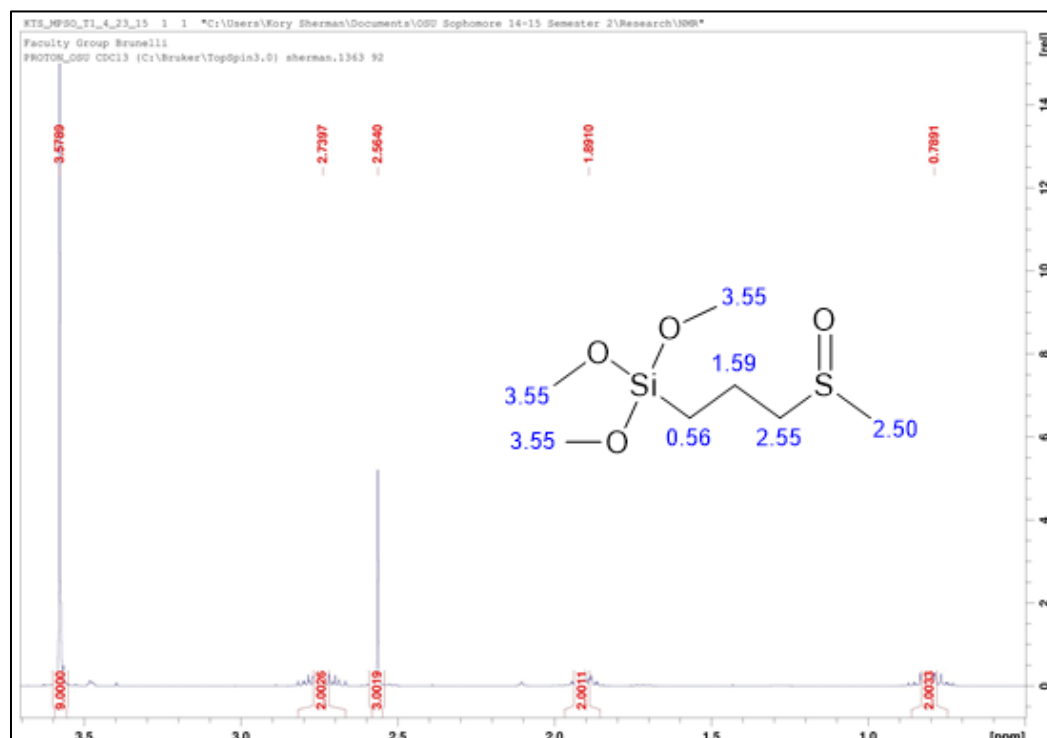
**Figure 6:** Functionalization strategy for the sulfonic group. The rightmost image illustrates Catalyst 1

To make the catalyst with analogues of both  $\text{H}_2\text{SO}_4$  and DMSO, a recently discovered organosilane was synthesized and functionalized to the silica surface via a “grafting to” approach, where the analogue is synthesized before functionalization onto the silica surface.<sup>9</sup> First, (3-mercaptopropyl)trimethoxysilane was reacted to form a thioether group, yielding methyl-3-trimethoxysilylpropylsulfide (MPS). This chemical was then partially oxidized to form methyl-3-trimethoxysilylpropylsulfoxide (MPSO), the DMSO analogue. Proton nuclear magnetic resonance was used to confirm successful synthesis of both MPS and MPSO. Figure 7 below displays the NMR for MPS, along with a MPS molecule with the corresponding chemical shifts labeled.



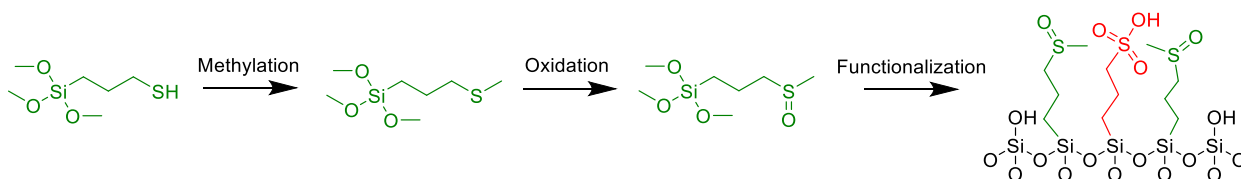
**Figure 7:**  $^1\text{H}$  NMR of synthesized MPS; the corresponding chemical shifts of each group are labeled on a MPS molecule

Moreover, Figure 8 below displays the NMR for MPSO, along with a MPSO molecule with the corresponding chemical shifts labeled.



**Figure 8:**  $^1\text{H}$  NMR of synthesized MPSO; the corresponding chemical shifts of each group are labeled on a MPSO molecule

Propylsulfonic acid-functionalized silica was then functionalized with this modified version of (3-mercaptopropyl)trimethoxysilane to produce the second catalyst with analogues of both  $\text{H}_2\text{SO}_4$  and DMSO (Catalyst 2). This procedure is illustrated below in Figure 9.



**Figure 9:** Functionalization strategy for the sulfoxide group. The rightmost image illustrates Catalyst 2

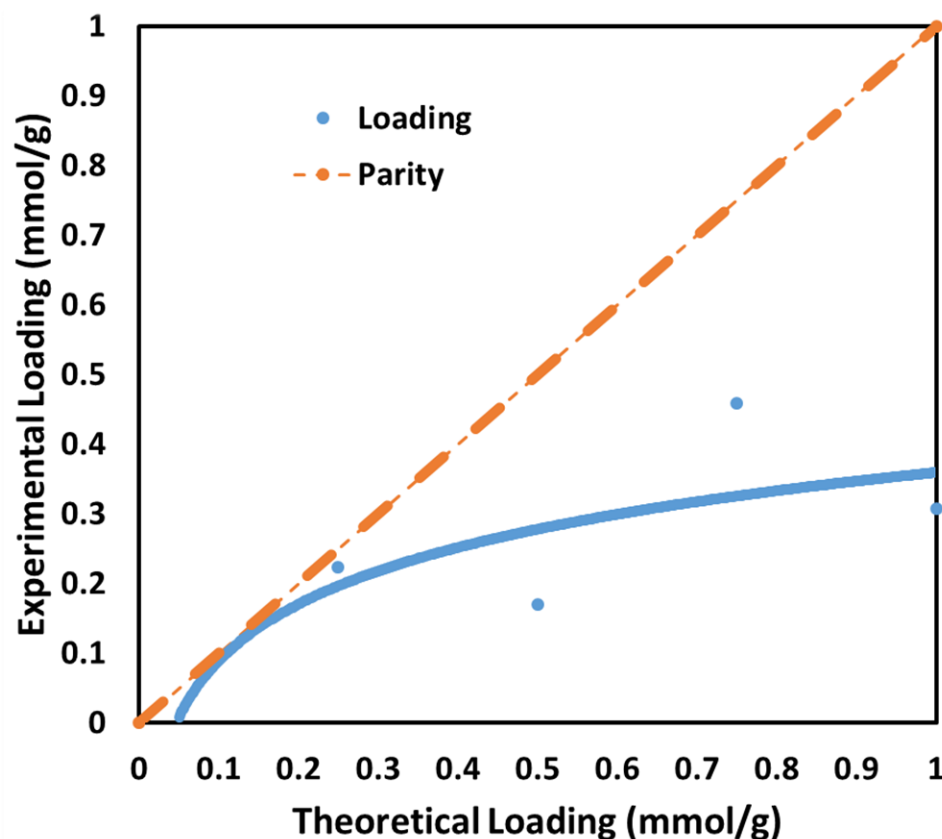


The second main component for this research involved catalyst characterization. The two catalysts were characterized through several methods including titration to determine acid site content, nitrogen physisorption, thermogravimetric analysis (TGA), High Performance Liquid Chromatography (HPLC), and proton nuclear magnetic resonance ( $^1\text{H}$  NMR). Characterization identifies key properties of the catalysts (i.e., acid site content) and is used to ensure that they are synthesized correctly. For applications of each characterization method, see Table 1 below.

**Table 1:** Uses of each characterization method that was utilized throughout this project

Equipment	Use
Titration	Determine acid site content and experimental loading of $\text{H}_2\text{SO}_4$ analogues on silica
Nitrogen Physisorption	Determine surface area and pore size distribution of silica
TGA	Quantifies the experimental loading of silica
$^1\text{H}$ NMR	Confirms chemical synthesis prior to functionalization
HPLC	Quantifies conversion of fructose and yield of HMF

Through titration, the experimental loading of sulfonic groups on the surface of each functionalized sample was determined and compared to theoretical loadings. The purpose of these tests was to establish whether there are any limitations on the loading of sulfonic groups on SBA-15. Figure 10 denotes the results of these tests.

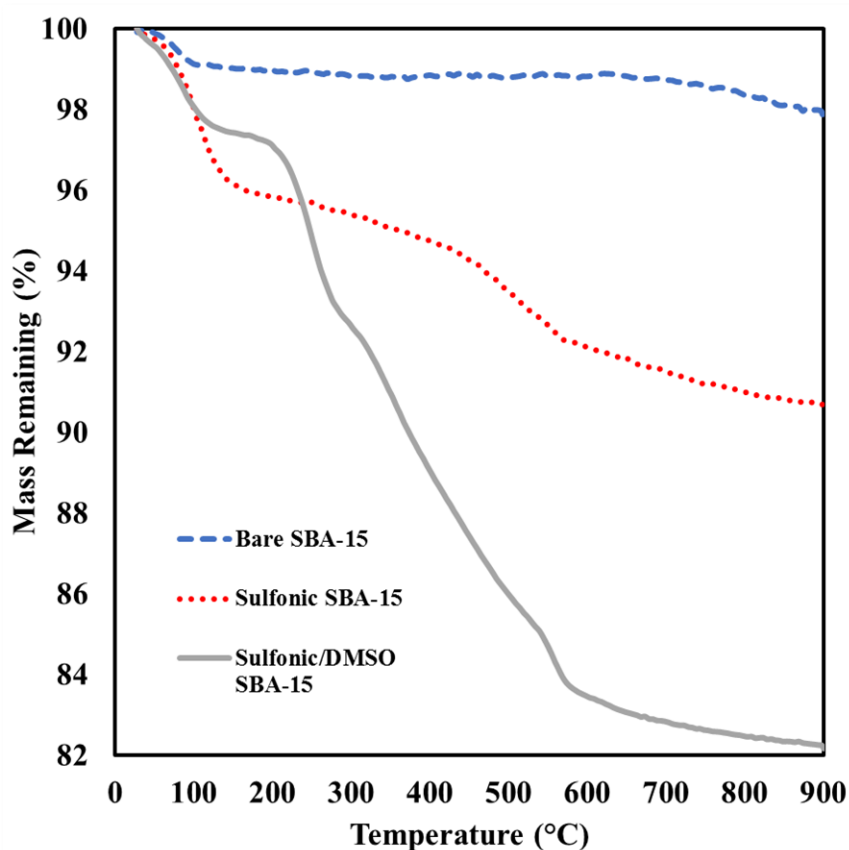


**Figure 10:** Experimental loading vs. theoretical loading of acid sites on SBA-15 silica functionalized with sulfonic acid analogues

As seen in Figure 10 above, testing showed that there were limitations to the possible loading of sulfonic groups onto the SBA-15. Overall, tests showed that the maximum experimental loading attainable was around 0.25 mmol/g. These results are also corroborated by previous experimentation.<sup>12</sup>

TGA operates through tracking the mass loss of a sample while continually heating it. In the case of functionalized SBA-15, as the temperature exceeds a certain point, the groups functionalized onto the surface become unstable and cleave from the silica surface, decreasing the overall mass of the sample. For this project, TGA was conducted for each catalyst after synthesizing the bare SBA-15 support, and after functionalizing products to its surface. For example, each bifunctional catalyst synthesized was sampled and taken for TGA three times: after

synthesizing the bare SBA-15, after functionalizing the  $\text{H}_2\text{SO}_4$  analogue onto the surface, and after additional functionalization of the DMSO analogue onto the surface. A graph illustrating the mass loss versus temperature for bare SBA-15, SBA-15 with  $\text{H}_2\text{SO}_4$  analogues functionalized onto the surface (Catalyst 1), and SBA-15 with  $\text{H}_2\text{SO}_4$  and DMSO analogues functionalized onto the surface (Catalyst 2) is shown below in Figure 11.

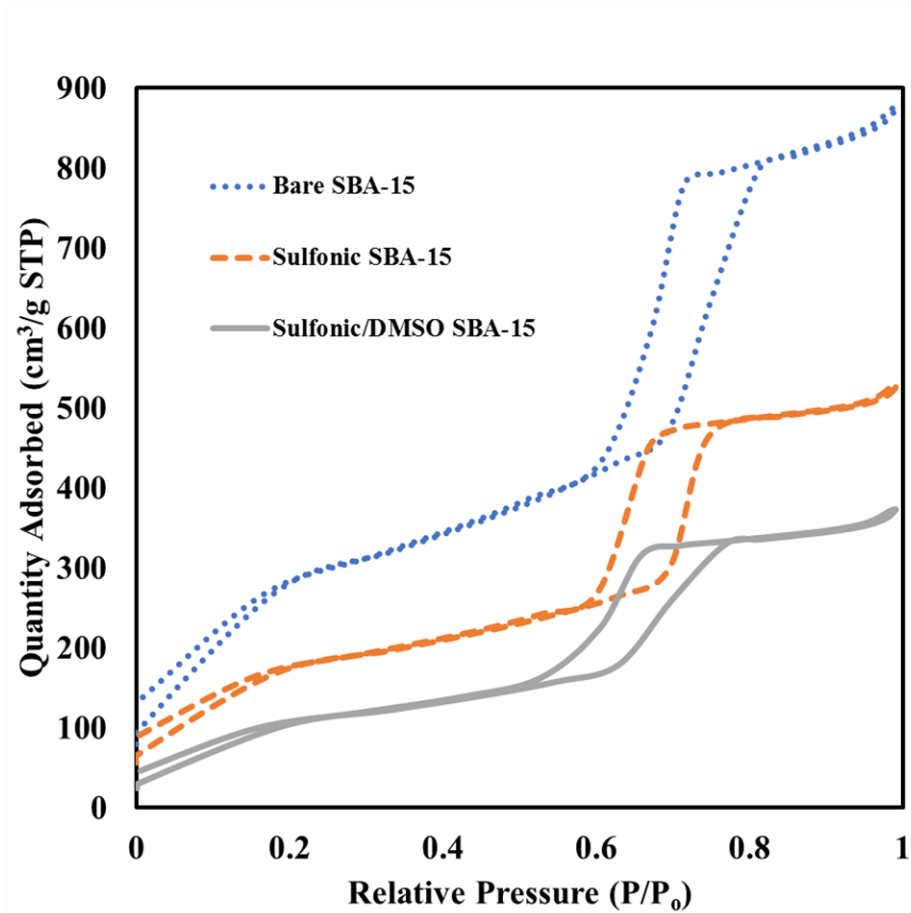


**Figure 11:** TGA mass loss versus temperature results of 3 tests using bare SBA-15, SBA-15 functionalized with SBA-15 with  $\text{H}_2\text{SO}_4$  analogues (Catalyst 1), and SBA-15 with  $\text{H}_2\text{SO}_4$  and DMSO analogues (Catalyst 2)

Looking at Figure 11, almost no mass loss was observed for the bare SBA-15 sample. This result was expected, as there were no groups functionalized onto the surface that could be easily removed via heating. For the SBA-15 sample functionalized with  $\text{H}_2\text{SO}_4$  analogues, almost 10% of its mass was lost over the entire heating period; this provided evidence that the  $\text{H}_2\text{SO}_4$  analogues were successfully functionalized, and when considering the initial mass of the sample allowed for

quantification of the amount of  $\text{H}_2\text{SO}_4$  analogues on the silica surface. Moreover, the greatest mass loss over the entire heating period was seen for the SBA-15 sample functionalized with  $\text{H}_2\text{SO}_4$  and DMSO analogues, as expected. In addition to providing evidence that DMSO analogues were successfully synthesized onto the silica surface, the difference in mass loss between the SBA-15 sample functionalized with  $\text{H}_2\text{SO}_4$  and DMSO analogues and the sample functionalized with only  $\text{H}_2\text{SO}_4$  analogues could be used to quantify the loading of the DMSO analogues onto the silica surface (after correcting for differences in initial sample mass).

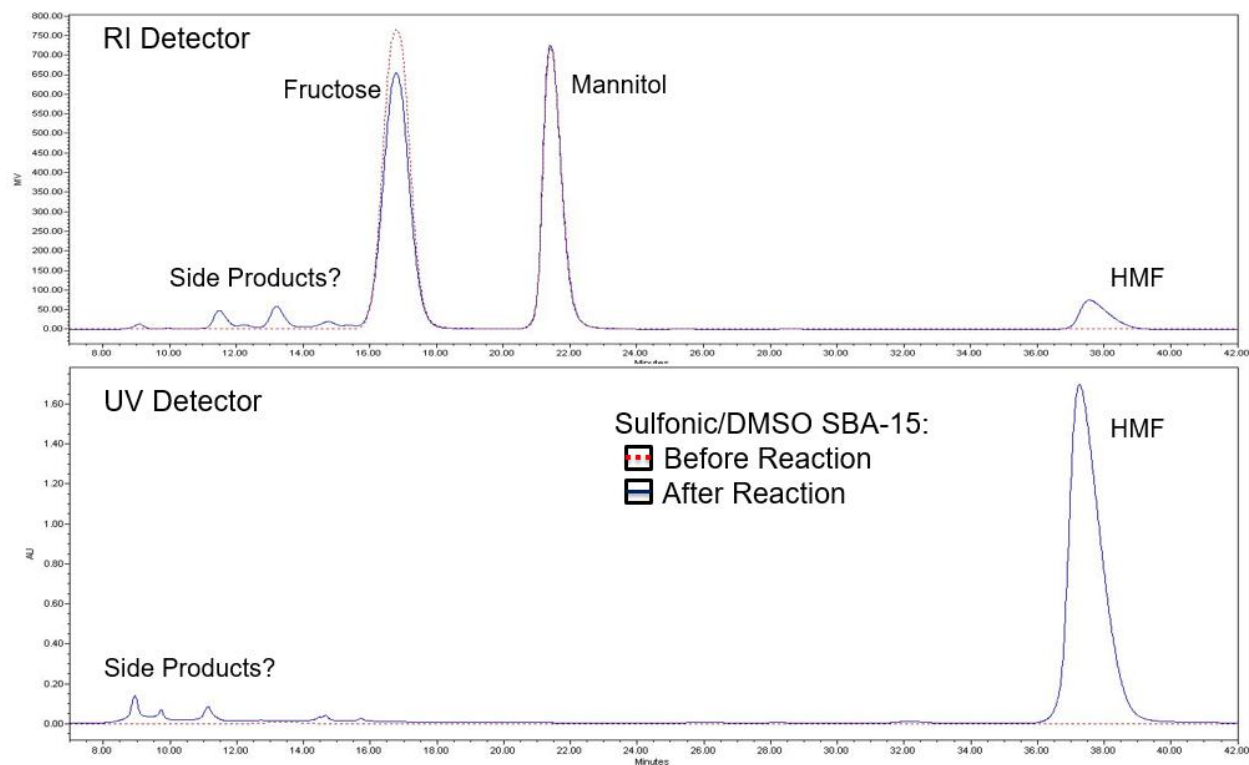
Nitrogen Physisorption was used to quantify surface area, pore size, and pore distribution of SBA-15 samples before and after being functionalized with the sulfonic analogue and the sulfoxide analogue. An example of isotherm plots generated for bare SBA-15, SBA-15 functionalized with  $\text{H}_2\text{SO}_4$  analogues, and SBA-15 functionalized with both  $\text{H}_2\text{SO}_4$  and DMSO analogues is illustrated in Figure 12.



**Figure 12:** Isotherm linear plot of bare SBA-15, SBA-15 functionalized with sulfonic analogues, and SBA-15 functionalized with both sulfonic and sulfoxide analogues. The differences between quantity absorbed for each sample is related to their respective level of functionalization.

Examining the adsorption and desorption curves in Figure 12, hysteresis is observed between the expected region for mesoporous silica. Moreover, the isotherm is Type IV, further substantiating that the SBA-15 sample is mesoporous. The type of hysteresis loop indicates that, overall, the material consists of well-defined cylindrical-like pore channels; however, the horizontality of the hysteresis loop indicates that there may be some level of disorder, as some pores on the sample may not be well-defined. Also, a decrease in quantity absorbed between the bare SBA-15 sample, SBA-15 sample functionalized with sulfonic analogues only, and SBA-15 sample functionalized with sulfonic and sulfoxide analogues, respectively, further supports that the sulfonic and sulfoxide groups were appropriately functionalized onto the silica surface.

The final component of this research was catalytic testing. The catalysts were used in a dehydration reaction with fructose and a solvent to determine their effectiveness in promoting the formation of HMF. The first two of four reaction sets that were performed and analyzed were Catalyst 1 with fructose and water and Catalyst 1 with fructose and a water/DMSO mixture. The selectivity and yield of HMF for these two reactions were previously tested and reported in other publications, but it was important to repeat these reactions as control experiments. More specifically, Catalyst 1 with fructose in a water/DMSO mixture was tested and analyzed to help decipher if any of the properties of the bifunctional catalyst can be altered to help optimize the selectivity and yield of HMF. The third reaction tested, and the focus of this research, was Catalyst 2 with fructose and water. The results of these reactions were quantified using high-performance liquid chromatography (HPLC). When using HPLC, the refractive index (RI) detector was used to track the disappearance of fructose, and the ultraviolet (UV) detector was used to track the production of HMF. While running HPLC tests, mannitol was used as an inert external standard; a known mannitol concentration between different tests was used to substantiate results obtained using the device. Internal standards were also created for fructose and HMF through creating graphs of peak integration area versus known concentration. An example of an HPLC chromatogram, with fructose, HMF, and mannitol concentrations before and after the reaction denoted, is shown in Figure 13.



**Figure 13:** HPLC chromatographs depicting reactant and product concentrations before and after a reaction

The selectivity and yield of HMF in each experiment was compared to the state-of-the-art commercial catalyst, Amberlyst-15. When Amberlyst-15 is used as a catalyst for the dehydration reaction of fructose in DMSO, HMF yields can be upwards of 80%.<sup>10</sup> Because it is a commercially available product, it is currently thought to be the most accessible and efficient catalyst in terms of HMF yield and selectivity for this reaction.

### 3. Results and Discussion

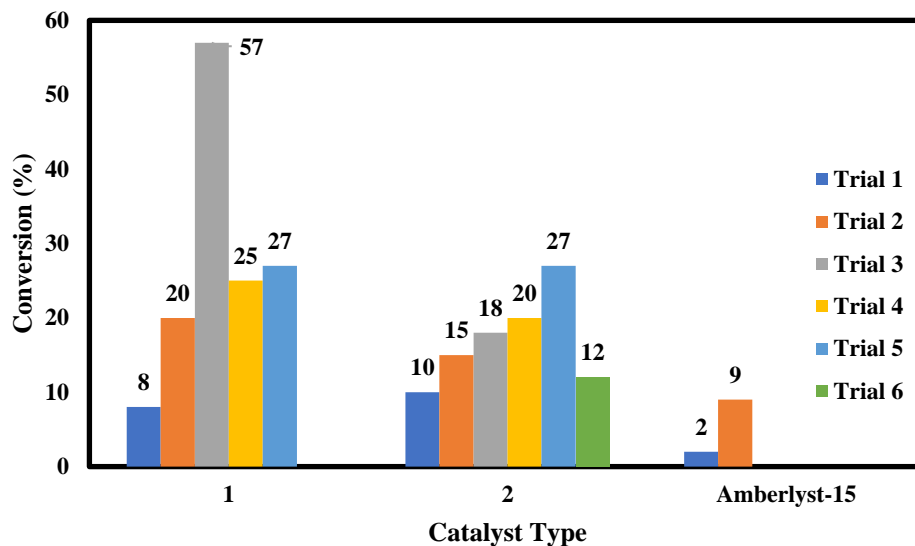
Catalyst 1 and Catalyst 2 were synthesized and tested while varying mole percent of catalyst to solvent, sulfonic group loading, and reaction solvent. For comparison, two tests using Amberlyst-15 were also performed. All tests were run at 120°C for 24 hours and mixing was accomplished using a magnetic stir bar spinning at 420 rpm. A summary of the critical experimental results is tabulated below in Table 2. The naming convention for each catalyst in Table 2 includes the catalytic support type (all samples use ‘SBA’ to denote SBA-15), the loading of the sulfonic acid analogues on the silica surface (mmol/g) following the letters ‘SA’, and, if applicable, the loading of the DMSO analogues on the silica surface (mmol/g) following the letters ‘DMSO’. If two different catalysts have the same catalytic support type, sulfonic acid analogue loading, and DMSO analogue loading, ‘V’ followed by a number denoting the order in which each catalyst was synthesized is present at the end of each applicable catalyst’s name.

**Table 2:** Experimental results of catalytic testing with multiple versions of Catalyst 1, Catalyst 2, and Amberlyst-15. The solvent, mole percentage of catalyst used in the reaction, and loading of the sulfonic group for each catalyst are noted. The conversion of fructose and selectivity of HMF for each reaction was verified using HPLC testing, which included both internal and external standards. <sup>1</sup>The 50:50 Water:DMSO mixture is by volume.

Catalyst	Trial	Solvent	Mol % Catalyst	Sulfonic Group Loading (mmol/g)	Fructose Conversion (%)	HMF Selectivity (%)
SBA-SA0.25	1	Water	0.75	0.25	8	144
SBA-SA0.25	2	Water	0.75	0.25	20	27
SBA-SA0.25	3	Water/DMSO (50:50) <sup>1</sup>	0.75	0.25	57	91
SBA-SA0.25	4	Water	0.75	0.25	25	34
SBA-SA0.5	5	Water	2.5	0.5	27	48
SBA-SA0.25-DMSO1.0	1	Water	0.75	0.25	10	60
SBA-SA0.5-DMSO1.0-V1	2	Water	0.75	0.5	15	86
SBA-SA0.5-DMSO1.0-V2	3	Water	0.75	0.5	18	75
SBA-SA0.25-DMSO1.0	4	Water	2.5	0.25	20	73
SBA-SA0.5-DMSO1.1	5	Water	2.5	0.5	27	50
SBA-SA0.55-DMSO1.1	6	Water	2.5	0.5	12	57
Amberlyst-15	1	Water	2.5	-	2	143
Amberlyst-15	2	Water	2.5	-	9	71



After each reaction was completed, the conversion of fructose for each sample was quantified using HPLC and referencing standardized values. Figure 14 below illustrates the conversion achieved in each reaction.



**Figure 14:** Fructose conversion versus catalyst type for all catalytic tests. Tests are separated by catalyst type (Catalyst 1, Catalyst 2, Amberlyst-15), and the trial number for each catalyst type corresponds to the values noted in Table 2.

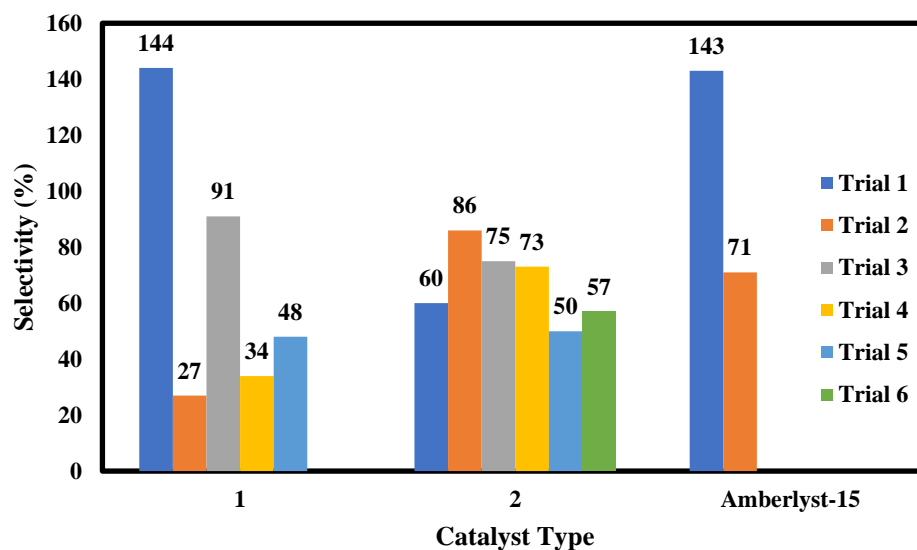
The highest conversion, 57%, was achieved during the third trial for Catalyst 1. This trial was completed using a 50:50 mixture by volume of water and DMSO as the solvent. When DMSO is used as the solvent, its maximum benefit is realized in terms of increasing the conversion of fructose and increasing the selectivity of HMF. Thus, this reaction was used as a measure of how close the bifunctional catalysts containing both DMSO and H<sub>2</sub>SO<sub>4</sub> analogues, reacting only in water, were to the maximum attainable conversion.

Overall, tests with Catalyst 1 and Catalyst 2 produced similar conversion levels of fructose. The highest fructose conversion, seen in both samples, was 27%. The average fructose conversion

for trials using Catalyst 1 and Catalyst 2 with water as the solvent was approximately 18%. Meanwhile, when Amberlyst-15 was use as the catalyst, the average conversion was significantly lower at approximately 5%.

The results show that Catalysts 1 and Catalyst 2 can reach significantly higher conversion levels for fructose compared to Amberlyst-15. As high fructose conversion is one of the critical barriers to the sustainability of this reaction, Catalyst 1 and Catalyst 2 both provide evidence that utilizing a catalyst incorporating groups functionalized to a SBA-15 silica support can improve the conversion of fructose in this reaction.

Furthermore, the selectivity of HMF was quantified and analyzed for each catalytic test. The results are summarized below in Figure 15.



**Figure 15:** HMF selectivity versus catalyst type for all catalytic tests. Tests are separated by catalyst type (Catalyst 1, Catalyst 2, Amberlyst-15), and the trial number for each catalyst type corresponds to the values noted in Table 2.

Looking at the results in Figure 15, it is apparent that Trial 1 for Catalyst 1 and Trial 1 for Amberlyst-15 should be excluded from analysis due to calculated selectivity levels exceeding 100%. Errors in experimental technique are thought to be attributed to these errors. When

performing small-scale catalytic tests, as in this case, small errors can be easily magnified to produce unreasonable results. Although the exact selectivity levels cannot be quantified, these trials seem to provide evidence that these catalysts offer at least some level of selectivity in regards to HMF for this reaction.

Considering the other trials, the selectivity of HMF when using Amberlyst-15 was similar to values seen in literature. Trials involving Catalyst 1 attained selectivity levels of HMF between approximately 20-50%. These results also align with values from literature for HMF selectivity when fructose is reacted in water, and  $\text{H}_2\text{SO}_4$  is included in solution as the catalyst. The similarity in HMF selectivity between the tests incorporating Catalyst 1 and the tests seen in literature provides encouraging evidence that the effectiveness and efficiency of the  $\text{H}_2\text{SO}_4$  analogues are not hindered by their functionalization onto the surface of Catalyst 1. The findings show that the  $\text{H}_2\text{SO}_4$  analogues on the silica surface are still able to catalyze the reaction and achieve similar selectivity levels compared to when  $\text{H}_2\text{SO}_4$  is combined with the solvent and free to move throughout the solution. Moreover, this further substantiates that functionalized SBA-15 silica can be used constructively under these reaction conditions.

Tests utilizing Catalyst 2 with water as the solvent, the focus of our research, showed encouraging results in regards to selectivity of HMF. The highest selectivity reached was 86%, and the average selectivity over the six runs was 67%. The increase in selectivity of Catalyst 2, compared to Catalyst 1, provides evidence that Catalyst 2 has additional functional groups on its surface (i.e., DMSO analogues). Thus, the results show that it is possible to functionalize DMSO analogues onto SBA-15 silica that has previously been functionalized with  $\text{H}_2\text{SO}_4$  analogues.

Although a substantial increase in selectivity was observed when using Catalyst 2 in relation to Catalyst 1, the selectivity of Catalyst 2 did not reach levels observed when a mixture of

water and DMSO was used as the solvent, as seen in literature and Trial 3 for catalyst SBA-SA0.25 (shown in Table 2). To verify the selectivity of HMF seen in literature when a water and DMSO mixture is used as the solvent, a test was run using Catalyst 1 and a 50:50 water:DMSO mixture by volume as the solvent. This trial resulted in a 91% selectivity of HMF. Because the selectivity in the trial using Catalyst 1 and a 50:50 water:DMSO mixture as the solvent was greater than the selectivity seen when using Catalyst 2 with water as the solvent, this indicates that the beneficial effects of DMSO are not being fully exploited when Catalyst 2 is used. Functionalizing DMSO analogues to the silica surface are thought to be limiting the DMSO analogue's ability to solvate HMF and prevent undesirable side reactions, compared to when DMSO molecules are free to move throughout the reaction solution. This is thought to be a consequence of the limited mobility of the DMSO analogues when functionalized onto the silica surface.

Although the selectivity when using Catalyst 2 with water as the solvent was not found to produce selectivity levels as high as when DMSO is in solution, the results show that incorporating  $\text{H}_2\text{SO}_4$  and DMSO analogues on the surface of SBA-15 allows their beneficial effects, that are observed when they are in solution, to be utilized when they are functionalized onto a solid catalyst support in water. Overall, these tests serve to further substantiate the viability of using a bifunctional catalyst, incorporating  $\text{H}_2\text{SO}_4$  and DMSO analogues on its surface, in the dehydration reaction of fructose in water to increase the conversion and selectivity of HMF in an energy-efficient, environmentally friendly, and sustainable manner.

#### 4. Conclusions and Future Work

The primary objective of this research was to investigate the plausibility of using a bifunctional catalyst that contains analogues of  $\text{H}_2\text{SO}_4$  and DMSO as an energy-efficient, environmentally friendly method to achieve a high conversion and selectivity of HMF in the dehydration reaction of fructose in water. Multiple catalysts, using SBA-15 as the support, were synthesized and tested, including a catalyst functionalized with  $\text{H}_2\text{SO}_4$  analogues (Catalyst 1) and a bifunctional catalyst incorporating  $\text{H}_2\text{SO}_4$  and DMSO analogues (Catalyst 2). Amberlyst-15, a commercially available catalyst, was also tested for comparison.

Trials with Catalyst 1 in water showed selectivity levels of HMF that align with literature values when fructose is reacted in a solution of water and  $\text{H}_2\text{SO}_4$ . This provides evidence that molecules in solution can be functionalized onto a SBA-15 silica support, effectively catalyze a reaction, and reach selectivity levels similar to when  $\text{H}_2\text{SO}_4$  is in solution. Trials with Catalyst 2 in water showed much improved selectivity levels compared to Catalyst 1 in water, albeit with selectivity levels lower than when DMSO is in the reaction solution.

It is thought that the selectivity of HMF when using a bifunctional catalyst incorporating  $\text{H}_2\text{SO}_4$  and DMSO analogues can be improved through fine-tuning of the catalyst and reaction environment. One hypothesis is that optimizing the linker length of the carbon bonds joining the analogues to the catalyst surface can improve selectivity. Increasing the DMSO linker length may give those groups on the surface a greater ability and range to which they can move and solvate HMF molecules, thus inhibiting further undesirable reactions. On the other hand, it is thought that decreasing the length of the alkyl linker on the sulfonic group can benefit reaction selectivity through preventing organic leaching. Another proposition is creating a molecule containing two sulfoxide groups per organosilane. It is thought that these transformed DMSO analogues can

improve conversion and selectivity through increasing the density of sulfoxide sites on the catalyst surface, thus improving the likelihood that these DMSO analogues are able to solvate all of the HMF molecules present, and in turn minimize the amount of undesirable side products that form.

On a greater level, these trials and results have shown that molecules used in a reaction solution to promote the conversion and selectivity of a desired product can be functionalized onto a solid catalytic surface. This catalyst, then, can then be placed in a reaction solution that is absent of these molecules, and the reaction can proceed while still taking advantage of the beneficial effects of these molecules when they are functionalized on the catalyst surface. Therefore, the overarching principals observed in this experiment have the potential to be extended to similar conditions, opening a gateway to developing additional bifunctional catalysts incorporating solvent-like molecules, and in turn creating more efficient, cost-effective, and eco-friendly reactions.

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